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July 31, 2009

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Moisture Outgassing Rates from TATB-Formulations: Experiments and Kinetic Model Development

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Introduction

Moisture outgassing rates from materials are of interest and importance to a variety of different fields. Because water can attack and accelerate decomposition, aging, or rusting of various parts, the assembly of an apparatus with "wet" materials can shorten the lifetime of the apparatus. Outgassing of moisture from materials can be quite slow and a material that is seemingly dry at the time of assembly may slowly release water over years. This slow release of water will compromise the other constituents of the apparatus (e.g. electrical components, metals, organic materials) and shorten the lifetime of the apparatus. For apparatuses that are expensive or laborious to construct, it is especially important to understand and be able to predict the mechanisms and rates of water release from various materials. Such an understanding can support the development of accurate estimates of the apparatus's serviceable age and may allow for mitigation strategies in order to protect other parts from water.

Energetic materials such as TATB based PBX-9502 (95% TATB, 5% Kel-F 800) and LX-17 (92.5% TATB and 7.5% Kel-F) pose a particularly challenging problem because they are heterogeneous materials with potentially many different sources and mechanisms of water release. Water molecules could be adsorbed into the polymeric binder matrix, trapped in occlusions within the polymer and the TATB crystals/particles, or trapped within defect sites in the TATB crystal. Finally, many studies indicate that water is a decomposition product under rapid heating conditions, at high temperatures and/or high pressure.[2-6]

Previous studies have measured the water release rate(s) from LX-17 or PBX-9502 prill/powder in order to establish oven drying times prior to use. These studies limited their time frame to a few days or a week of drying.[1,7] Other studies have looked at the rate of water release of large pressed parts contained in sealed containers. [8,9] Finally, some studies have looked at the rate of water diffusion through pressed parts,[10-12] or the effects of wet vs. dry machining,[13,14] or the influence of the synthesis methods in the amount of water present.[1]

There are a few different models that have been developed to predict the rate of water release from LX-17 or PBX-9502.[1,15] These models are, to some extent, limited by the limitations of the experiments. Because all these experiments looked at water release over a relatively short period of time and left the samples relatively undamaged, they serve as a lower bound.

In this work, we perform experiments and develop models that can serve as an upper bound on the rate and amount of water that can be released. Our experimental approach is to use temperature programmed desorption (TPD) and monitor the rate and amount of water release as a function of temperature. We analyzed our experimental data using two different kinetic analysis methods (isoconversional analysis and nth-order Arrhenius

kinetic fits) and used the results to make predictions. The suitability of these kinetic analysis methods as well as the applicability of these experiments to long term aging (e.g. years) issues are discussed. Using the kinetics from our experiments, we predict the water release at temperature and timescales relevant to the existing literature. Based on our analysis and comparison with older data, the kinetic model(s) developed in this work serve as a relatively accurate (i.e. order of magnitude) method for predicting the water release under a variety of thermal histories.

Experimental

For a typical TPD experiment, PBX-9502 powder (< 10 mg) was wrapped inside a Pt foil envelope. The side of the envelope facing the mass spectrometer was perforated with pin holes over its entire surface. The loaded foil was attached to a sample holder by way of mechanical clamps and transferred into an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-6} Pa (4 x 10^{-7} Pa in the mass spectrometer chamber) through a differentially pumped load lock. The sample temperature was measured using a type K thermocouple inserted between the Pt envelope front surface and one of the clamps holding the envelope. The sample was then pumped in the UHV chamber for 3 hours to remove H_2O molecules that were loosely bonded to the powder. Heating of the samples was done by passing current through a tungsten coil located 2 mm behind the samples. Samples were heated at five different heating rates (0.005 C/s, 0.0075 C/s, 0.0125 C/s, 0.025 C/s and 0.15 C/s). The detector chamber is equipped with a quadruple mass spectrometer (QMS) and has been described in detail elsewhere. [16]

The water outgassing kinetics were obtained via two different kinetic analysis methods, the isoconversional method by Friedman and a simple nth-order Arrhenius analysis. Both methods are described in detail in the literature.[17-19]Briefly, in both methods the rate equation for fraction reacted begins with:

$$\frac{d\alpha}{dt} = kf(\alpha) = Ae^{-E/RT}f(\alpha) \tag{1}$$

where α is fraction reacted (0-1), t is time, k is the Arrhenius rate constant, E is the activation energy, R is the gas constant, T is temperature, and $f(\alpha)$ is the reaction model. In the Friedman isoconversional method, equation (1) is rearranged to the following:

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = \frac{-E_\alpha}{RT_\alpha} + \ln[A_\alpha f(\alpha)] \tag{2}$$

By plotting $\ln(d\alpha/dt)$ versus $1/T_\alpha$ (i.e. the temperature at each fraction point, α) and fitting the data to a line, the values for E_α and $\ln\{A_\alpha f(\alpha)\}$ can be calculated. These values are dependent on the extent of the reaction. To make a prediction at a chosen isothermal temperature (T_o) one must simply integrate equation (1) and use the values for E_α and $\ln\{A_\alpha f(\alpha)\}$ from equation (2). The time integral at isothermal temperature is:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^\alpha \frac{d\alpha}{[A_\alpha f(\alpha)]e^{-E_\alpha/RT_o}} \tag{3}$$

In the nth-order Arrhenius analysis, a bi-Arrhenius form of equation (1) was used:

$$\frac{d\alpha}{dt} = k_1 f_1(\alpha)w_1 + k_2 f_2(\alpha)w_2 = A_1 e^{-E_1/RT}\alpha^{n_1}w_1 + A_2 e^{-E_2/RT}\alpha^{n_2}w_2 \tag{4}$$

where the subscript numbers are used for indexing purposes only and *w* corresponds to a weighting factor. To make a prediction using this model, one must simply apply the derived kinetic parameters from a prior fit (i.e. A, E, and n) and introduce the desired temperature or temperature profile. Fits and predictions using the nth-order Arrhenius model were performed using the program Kinetics05.[20]

Results and Discussion

Figure 1 shows the fraction of water released (α) as a function of temperature as measured in the TPD experiment. It is clear in this figure that there are two regimes. At lower temperatures (< 125 °C) the water release accelerates then stabilizes to a steady rate. The majority of the water is released at the higher temperatures. These two distinct regimes are probably due to different mechanisms of water release. One might speculate that the anisotropic expansion of TATB or sublimation of the material may be two possible mechanisms. More work is necessary to understand the mechanisms.
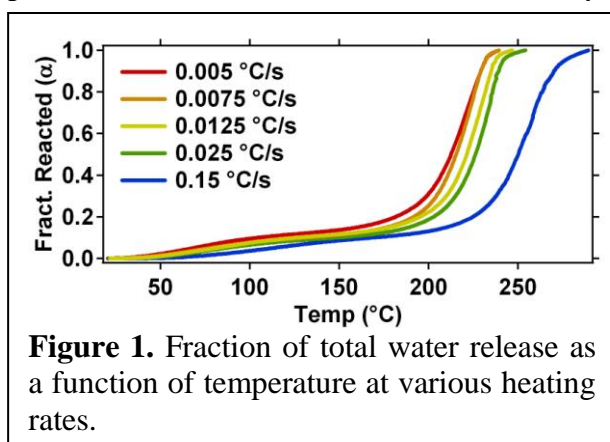

Figure 1. Fraction of total water release as a function of temperature at various heating rates.

Two different kinetic analysis methods were applied to this data, the nth-order Arrhenius model and Friedman's isoconversional model. The kinetic parameters from the nth-order Arrhenius model are listed in Table 1. Because of the two distinct regimes observed in Figure 1, the data was fit to a bi-modal kinetic model consisting of two rates and two sets of Arrhenius parameters. As expected, the first activation barrier (E) is lower than the second; however, the first frequency factor (A) is also quite a bit lower than the second. Typically, a higher frequency factor results in an accelerated rate; hence a low frequency factor will attenuate the effects of a low activation barrier. It is noteworthy that the reaction order (n) for the first reaction is quite large relative to the second; these reaction orders may provide clues to the mechanisms underlying these two kinetic regimes. In general, the fits of the model to the data were quite good, indicating that the kinetic parameters accurately represent the data.

The results of the isoconversional analysis are shown in Figure 2. Because this analysis method provides a fractional dependent activation energy and value for ln{Af(α))} this data can only be accurately presented in a figure, not a table. According to the results in Figure 2, the activation energy drops during the first 10% of the reaction and then rises again up to the 20% mark. Between 20% and 80% the activation energy is relatively stable and is quite similar to the second activation energy in our nth-order fit (Table 1, index 2).

Table 1. Arrhenius parameters for an nth-order fit to the fraction of moisture outgassing as a function of temperature. Refer to equation 4 for an explanation of variables.

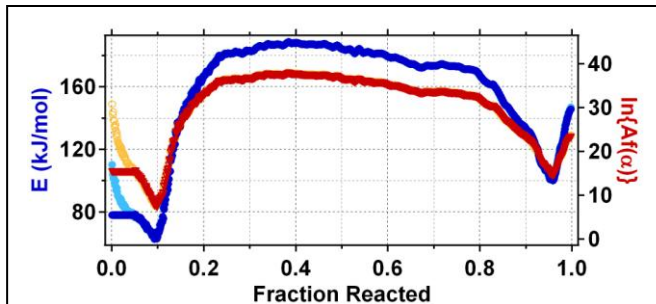|	Index 1	Index 2
A (1/s)	2.5E+07	8.3E+15
E (kJ/mol)	72	180
n	5.8	1
w	0.19	0.81

Figure 2. Isoconversional fit parameters as a function of fraction reacted. Light blue and orange lines indicate the values of E and ln{Af(a)}, respectively, prior to cropping the first 5% of the reaction. Refer to the text for a full discussion.

a specific fraction reacted, i.e., α. In contrast, the nth-order Arrhenius model must fit the data over a range of α's in order to back out a single set of kinetic parameters, which raises the question of whether the mechanisms at higher temperatures are the same as lower temperatures. Ultimately, the biggest concern for both of these models is whether the mechanisms of water release under these temperatures and pressures can be extrapolated down to milder temperatures and pressures. One limitation of the isoconversional analysis method is that the first 5-10% of the reaction will have questionable fit parameters because of the tendency for the term $\ln(d\alpha/dt)$ to blow up at the lowest values of α. Due to this limitation we have eliminated the fit parameters in the first 5% of the reaction and assumed constant values between 0 and 5%.

Figure 3 compares the results of an oven drying test to predictions from the isoconversional analysis and the nth-order Arrhenius model. In the oven drying test, LX-17 molding powder was laid out in a drying tray at a thickness of 1.5-2 in and placed in preheated ovens (90, 100, and 120 °C). Samples were extracted from the trays periodically between 2 and 96 hours and stored in glass vials until they were analyzed using the Karl-Fischer method.
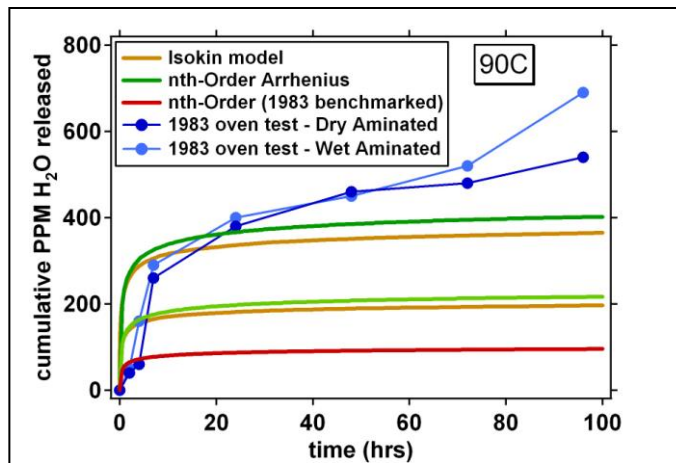

Figure 3. Comparison of isoconversional (brown lines) and nth-order Arrhenius model (green lines) predictions to oven drying test results by Stull et al. (blue points/lines). The red line corresponds to the nth-order model adjusted to the maximum water content measured in Stull.[1]

Comparison of the experimental results with the model predictions in Figure 3 indicate that both models do a reasonable job of predicting the amount and rate of water release. These models are best suited for predicting the *relative* population of water

released as a function of the thermal history; the *actual* amount of water released depends on the initial concentration. In Figure 3, the two lines associated with each model correspond to a maximum and minimum, and are dependent on the total amount of water released in the TPD experiments. When the initial concentration of water from Stull's experiments was used with the nth-order Arrhenius model, the resulting prediction (red line in Figure 3) does not match the experimental data. One likely explanation is that Stull's method of measuring water content may have a systematic error. In the Karl-Fischer method, solid samples are dispersed or dissolved in a nonaqueous solvent and water is titrated.[21] It is well known that TATB has very low solubility in most solvents,[22] hence a method was developed in which the TATB-formulations were dispersed into a solvent via a Waring blender.[21] The method developers acknowledged the fact fine particles settle out of the suspension and that this method, while precise, has not been proven to be accurate.[21] We surmise that the fine precipitate particles may still have water trapped in them and that the Karl-Fischer method may not be able to accurately measure the total concentration of water. In general, this may not be an issue as most aging scenarios will not be able to access the deeply imbedded water; however, care must still be taken when comparing total moisture content from TPD experiments versus Karl-Fischer analysis.

Both the isoconversional model and the nth-order Arrhenius model were compared to a number of other sets of experimental data. In all cases, the rate of water release was similar between the models and the experiments; however, the actual amount of water varied due to variability in initial water content.

Conclusions

A kinetic model such as the isoconversional or nth-order model, which is based on a highly accurate measurement of water release as a function of time, can be extremely useful in predicting various thermal scenarios. Most important, however, is an accurate measurement of the initial concentration of water in the sample. Our TPD experiments may provide a more accurate measurement of water release rates as well as absolute water concentration in a sample; therefore, they serve as an upper bound on the rate and amount of water that can be released. Using our models, water release can be predicted for a variety of different thermal histories. Both models are well suited to investigating a wide range of temperatures and timescales, as they both allow for multiple barriers.

Acknowledgement.

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